

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A61K 7/075	A1	(11) International Publication Number: WO 97/35549 (43) International Publication Date: 2 October 1997 (02.10.97)
(21) International Application Number: PCT/US97/03698 (22) International Filing Date: 18 March 1997 (18.03.97) (30) Priority Data: 08/624,016 27 March 1996 (27.03.96) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: GUSKEY, Susan, Marie; 10758 Moss Hill Lane, Montgomery, OH 45249 (US). SCHRADER, Elizabeth, Murphy; 214 Dogwood Drive, Loveland, OH 45140 (US). WELLS, Robert, Lee; 4245 Rose Hill Avenue, Cincinnati, OH 45229 (US). BARAVETTO, John, Thomas; 3741 Mon- ets Lane, Cincinnati, OH 45241 (US). COFFINDAFFER, Timothy, Woodrow; 118 Bridle Lane, Loveland, OH 45140 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AU, BR, CA, CN, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: CONDITIONING SHAMPOO COMPOSITION (57) Abstract Disclosed are aqueous hair conditioning shampoo compositions comprising a specific surfactant component comprising an ethoxylated alkyl sulfate surfactant having from about 1 to about 8 moles of ethoxylation and an amphoteric surfactant in a shampoo with insoluble, dispersed conditioning agent, a low viscosity organic conditioning oil and a select soluble cellulosic cationic organic polymer hair conditioning agent.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

CONDITIONING SHAMPOO COMPOSITION

5

FIELD OF THE INVENTION

10 This invention relates to conditioning shampoo compositions containing a specific surfactant component comprising an ethoxylated alkyl sulfate surfactant having from about 1 to about 8 moles of ethoxylation and an amphoteric surfactant in a shampoo with insoluble, dispersed, nonionic conditioning agent, a low viscosity organic conditioning oil and a select soluble cellulosic cationic organic polymer hair conditioning agent. The compositions provide improved hair conditioning performance, including improved wet hair feel.

15

BACKGROUND OF THE INVENTION

Human hair becomes soiled due to its contact with the surrounding atmosphere and, to a greater extent, from sebum secreted by the head. The build-up of the sebum causes the hair to have a dirty feel and an unattractive appearance. The soiling of the hair necessitates it being shampooed with frequent regularity.

20

Shampooing the hair cleans by removing excess soil and sebum. However, the shampooing process has disadvantages in that the hair is left in a wet, tangled and generally unmanageable state. Shampooing can also result in the hair becoming dry or "frizzy", and a loss of luster, due to removal of natural oils or other hair moisturizing materials. After shampooing, the hair can also suffer from a loss of "softness" perceived by the user upon drying. The hair can also suffer from increased levels of static upon drying after shampooing. This can interfere with combing and can result in fly-away hair. A variety of approaches have been developed to alleviate the after-shampoo problems. These range from the inclusion of hair conditioning aids in shampoos to post-shampoo application of hair conditioners, i.e., hair rinses. Hair rinses are generally liquid in nature and must be applied in a separate step following the shampooing, left on the hair for a length of time, and rinsed with fresh water. This, of course, is time consuming and is not as convenient as shampoos containing both cleaning and hair conditioning ingredients.

25

30 While a wide variety of shampoos have been disclosed which contain conditioning aids, they have not been totally satisfactory for a variety of reasons. Cationic conditioning agents are highly desirable for use in hair conditioning due to their abilities to control static, improve wet detangling, and provide a silky wet hair feel to the user. One problem which has been encountered in shampoos relates to compatibility problems between good cleaning anionic surfactants and the many conventional cationic agents which

35

historically have been used as conditioning agents. Efforts have been made to minimize adverse interaction through the use of alternate surfactants and improved cationic conditioning agents. Cationic surfactants which provide good overall conditioning in hair rinse products, in general, tend to complex with anionic cleaning surfactants and provide poor conditioning in a shampoo context. In particular, the use of soluble cationic surfactants that form soluble ionic complexes do not deposit well on the hair. Soluble cationic surfactants that form insoluble ionic complexes deposit on the hair but do not provide good hair conditioning benefits, and tend to cause the hair to have a dirty, coated feel. The use of insoluble cationic surfactants, e.g., tricetyl methyl ammonium chloride, can provide excellent anti-static benefits but do not otherwise provide good overall conditioning. Many cationic polymers tend to build up on the hair to result in an undesirable, "unclean" coated feel. Cationic polymers therefore, conventionally, are preferably used at limited levels to minimize this problem. This, however, can limit the overall conditioning benefits that are obtained. Additionally, cationic conditioning agents commonly do not provide optimal overall conditioning benefits, particularly in the area of "softness", especially when delivered as an ingredient in a shampoo composition.

Materials which can provide increased softness are nonionic silicones. Silicones in shampoo compositions have been disclosed in a number of different publications. Such publications include U.S. Patent 2,826,551, Geen, issued March 11, 1958; U.S. Patent 3,964,500, Drakoff, issued June 22, 1976; U.S. Patent 4,364,837, Pader, issued December 21, 1982; and British Patent 849,433, Woolston, issued September 28, 1960. While these patents disclose silicone containing compositions, they also did not provide a totally satisfactory product in that it was difficult to maintain the silicone well dispersed and suspended in the product. Recently, stable, insoluble silicone-containing hair conditioning shampoo compositions have been described in U.S. Patent 4,741,855, Grote and Russell, issued May 3, 1988 and U.S. Patent 4,788,066, Bolich and Williams, issued November 29, 1988. These shampoo compositions can deliver excellent overall conditioning benefits to the hair while maintaining excellent cleaning performance, even with the use of anionic deterative surfactants, for a wide variety of hair types.

More recently, improved conditioning shampoos were provided in U.S. Serial No. 07/622,699, Robert L. Wells, filed December 5, 1990, now abandoned, and its continuation application Serial No. 07/778,765, filed October 21, 1991, wherein shampoos containing anionic surfactant, dispersed, insoluble silicone, and certain relatively low ionic strength cationic polymers (greater than about 0.4 meq./gm) were disclosed. These compositions provide excellent hair cleaning conditioning to a wide variety of hair types, especially including improved conditioning to hair damaged by color treatments, bleaching, permanents, etc.

Japanese Patent Application, Laid Open No. 56-72095, June 16, 1981, Hirota et al. (Kao Soap Corp.) also discloses shampoo containing cationic polymer and silicone conditioning agents. Still other

patent publications relating to shampoos with cationic agents and silicone include EPO Application Publication 0 413 417, published February 20, 1991, Hartnett et al.

Another approach to providing hair conditioning benefits to shampoo compositions has been to use materials which are oily to the touch. These materials provide improved luster and shine to the hair. Oily materials have also been combined with cationic materials in the shampoo formulations. Japanese Patent Application Showa 53-35902, laid open October 6, 1979 (Showa 54-129135), N. Uchino (Lion Yushi Co.), discloses hair treatment compositions containing cationic polymer, fatty acid salt, and at least 10% of an oily component for use before or after shampooing. Suitable oily components are hydrocarbons, higher alcohols, fatty acid esters, glycerides, and fatty acids. Japanese Patent Application 62 [1987]-327266, filed December 25, 1987, published July 4, 1989, laid open No. HEI 1[1987]-168612, Horie et al., discloses detergent compositions containing cationic surfactant and/or cationic polymer, anionic surfactant, and specific esters of the formula RCOOR' wherein R and R' are straight or branched chain alkyls.

In spite of these attempts to provide optimal combinations of cleaning ability and hair conditioning, it remains desirable to provide further improved hair conditioning shampoo compositions. For instance, it remains desirable to improve overall conditioning, and especially shine and luster, wet and dry combing, and dry hair feel, of hair treated with shampoo containing silicone and cationic material. For shampoos containing oily materials in combination with cationic materials, it remains desirable to improve overall conditioning, especially wet combing and detangling, dry combing, and dry hair feel. However merely increasing the level of one or both conditioning ingredients can result in adverse effects such as greasy hair feel and loss of fullness. It is desirable to improve conditioning without suffering from these drawbacks.

One attempt to do this is disclosed in EPO Patent Publication No. 0 413 416, published February 20, 1991, Robbins et al., which discloses shampoo containing aminosilicone, anionic surfactant, cationic surfactant, and a hydrocarbon component. These types of formulations would normally be expected to result in either excessive buildup of aminosilicone on the hair, and consequently greasy hair feel and loss of fullness, or a relatively limited degree of improvement due to intentional use of very low levels of aminosilicone to avoid such adverse effects. The cationic surfactants would have limited ability to condition the hair due to interaction with the anionic surfactant.

EPO Patent Application Publication No. 0 413 417, published February 20, 1991, discloses shampoo containing anionic surfactant, and conditioning agents such as insoluble silicone (preferably aminosilicone), cationic surfactant, polyethylenes, paraffins, microcrystalline waxes, C₁₈-C₃₆ fatty acids or triglycerides, high fatty alcohol esters of high fatty acids, and beeswax. Another patent document which discloses shampoo compositions and a variety of conditioning agents is U.S. Patent 3,964,500, Drakoff, issued June 22, 1976. This patent relates to shampoo containing silicone conditioner and a hair bodying agent selected from certain wood rosins, shellac, sucrose acetate isobutyrate, and cationic amino cellulose.

A recent approach to providing hair conditioning benefits to shampoo is described in U.S. Patent 5,085,857 (Reid et al.). The composition disclosed combines a surfactant system (selected from anionic, nonionic, or amphoteric, or mixtures thereof), cationic guar derived polymer, and nonvolatile silicone having particle size less than 2 microns. Without being limited by theory, Applicants have found that by
5 utilizing a select cationic cellulose derived polymer in place of the cationic guar derived polymer in a specific surfactant system, which optimizes the conditioning coacervate formed, the present invention results in significantly improved conditioning performance.

In spite of all these approaches and attempts to provide optimum combinations of shampoos and hair conditioners, it remains desirable to provide still improved conditioning shampoos. It has now been
10 found that improved overall conditioning can be achieved by combining a specific surfactant component comprising an ethoxylated alkyl sulfate surfactant having from about 1 to about 8 moles of ethoxylation and an amphoteric surfactant in a shampoo with insoluble, dispersed, nonionic conditioning agent, a low viscosity organic conditioning oil and a soluble cellulosic cationic organic polymer hair conditioning agent. These compositions can provide improved conditioning while reducing the level of undesirable side effects
15 that can result from increasing the level of conditioning agent in prior known conditioning systems. As discussed previously, a conditioning agent system containing too much silicone can result in silicone build up on the hair over repeated usages and to loss of fullness of the hair. Too much oil results in an oily feel and a loss of fullness of the hair. Too much cationic conditioning agent results in a coated, dirty feel of the hair. Now it has been found that the components of the present invention can provide improved overall
20 conditioning while minimizing the adverse effects of conditioning agent build-up that otherwise can be incurred upon increasing the levels of individual components in prior known conditioning systems. It has now been found that by adding a low viscosity organic conditioning oil increases the deposition of, e.g., silicone conditioners, and provides improved conditioning benefits such as wet and dry feel and combing.

It is an object of this invention to provide shampoo compositions, which can provide excellent
25 cleaning performance and improved levels of conditioning while minimizing any adverse side effects associated with build-up due to the use of excess conditioning agent.

It is also an object of this invention to provide a method for cleaning and conditioning the hair which can provide excellent cleaning in combination with improved conditioning, while minimizing adverse side effects associated with excess build-up of conditioning agent on the hair.

30 These objects will become apparent from the description which follows, as may other objects become apparent upon a reading of said description.

SUMMARY OF THE INVENTION

The present invention is directed to hair conditioning shampoo compositions comprising:

- 5
- a) from about 5.0% to about 50% of a surfactant component comprising: i) an ethoxylated alkyl sulfate surfactant having from about 1 to about 8 moles of ethoxylation; and ii) an amphoteric surfactant;
- b) from about 0.01% to about 3.0% of a cationic cellulosic polymer having a molecular weight of from about 400,000 to about 1,500,000 and charge density of from about 0.6 to about 3 meq/g.;
- 10 c) from about 0.005% to about 5% of a water insoluble non-volatile conditioning agent having an average particle size below about 4 microns;
- d) from about 0.05% to about 5%, by weight, of an organic, nonvolatile, water insoluble liquid which is solubilized in the surfactant component and having a viscosity of from about 1 to about 300 centipoise selected from the group consisting of hydrocarbon oils and fatty esters having a boiling point at ambient pressure of about 250° C or higher, and mixtures thereof; and
- 15 e) an aqueous carrier wherein said composition comprises less than about 5% of ethoxylated alkyl sulfate surfactant having less than 1 mole of ethoxylation. The shampoo compositions provide improved conditioning performance, including improved wet hair feel.

DETAILED DESCRIPTION OF THE INVENTION

The shampoo compositions of the present invention can comprise, consist of, or consist essentially of the essential elements and limitations of the invention described herein, as well any of the additional or optional ingredients, components, or limitations described herein.

20 All percentages, parts and ratios are based upon the total weight of the shampoo compositions of the present invention, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include carriers or by-products that may be included in commercially available materials, unless otherwise specified.

25 As used herein, the term "soluble" refers to any material that is sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% by weight of the material in water at 25°C. Conversely, the term "insoluble" refers to all other materials that are therefore not sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% by weight of the other material in water at 25°C.

30 As used herein, the term "liquid" refers to any visibly (by the naked eye) flowable fluid under ambient conditions (about 1 atmosphere of pressure at about 25°C)

The shampoo compositions of the present invention, including the essential and optional components thereof, are described in detail hereinafter.

Surfactant Component

Alkyl Ether Surfactant

The shampoo compositions of the present invention comprise from about 5.0% to about 50% of a
detergent surfactant component comprising: i) an ethoxylated alkyl sulfate surfactant having from about 1
5 to about 8 moles of ethoxylation; and ii) an amphoteric surfactant component to provide cleaning
performance to the composition and wherein said the resulting composition comprises less than about 5%,
preferably less than about 3% and most preferably less than about 2% of alkyl sulfate ethoxylated
surfactant having less than 1 mole of ethoxylation

The detergent surfactant component can optionally comprises additional detergent surfactants.
10 Such surfactants should be physically and chemically compatible with the essential components described
herein, or should not otherwise unduly impair product stability, aesthetics or performance.

Concentration of the surfactant component in the shampoo composition ranges from about 5% to
about 50%, preferably from about 8% to about 30%, more preferably from about 10% to about 25%, even
more preferably from about 12% to about 20%, by weight of the composition.

15 The alkyl ether sulfates have the formula: $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$, wherein R is alkyl or alkenyl
from about 8 to about 24 carbon atoms, x is 1 to 8, and M is a cation such as ammonium, alkanolamines,
such as triethanolamine, monovalent metals, such as sodium and potassium, and polyvalent metal cations,
such as magnesium, and calcium. The cation M, of the anionic detergent surfactant should be chosen such
that the detergent surfactant component is water soluble. Solubility will depend upon the particular anionic
20 detergent surfactants and cations chosen.

Preferably, R has from about 8 to about 18 carbon atoms, more preferably from about 10 to about
16 carbon atoms, most preferably from about 12 to about 14 carbon atoms in both the alkyl and alkyl ether
sulfates. The alkyl ether sulfates are typically made as condensation products of ethylene oxide and mono-
hydric alcohols having from about 8 to about 24 carbon atoms. The alcohols can be derived from fats, e.g.,
25 coconut oil, palm kernel or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived
from coconut oil or palm kernel are preferred herein. Such alcohols are reacted with between about 1 and
about 10, and especially about 3, molar proportions of ethylene oxide and the resulting mixture of
molecular species having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is
sulfated and neutralized.

30 Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said
mixture having an average alkyl chain length of from about 10 to about 16 carbon atoms and an average
degree of ethoxylation of from about 1 to about 4 moles of ethylene oxide.

Amphoteric Surfactant

Suitable amphoteric surfactant components for use in the shampoo composition herein include those
35 which are known for use in shampoo compositions or other personal care cleansing composition, and

which contain a group that is anionic at the pH of the shampoo composition. Concentration of such surfactant components in the shampoo composition preferably ranges from about 0.5 % to about 20%, preferably from about 1% to about 10%, more preferably from about 2% to about 5% by weight of the composition. Examples of amphoteric surfactants suitable for use in the shampoo composition herein are described in U.S. Patents 5,104,646 (Bolich Jr. et al.), U.S. Patent 5,106,609 (Bolich Jr. et al.), which descriptions are incorporated herein by reference. Examples of amphoteric deterative surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodecylaminopropane sulfonate, sodium lauryl sarcosinate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "MIRANOL"TM and described in U.S. Patent 2,528,378.

Other amphoterics, sometimes classified as zwitterionics, such as betaines can also be useful in the present invention. Such zwitterionics are considered as amphoterics in the present invention where the zwitterionic has an attached group that is anionic at the pH of the composition. Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, cocoamidopropyl betaine, cocobetaine, lauryl amidopropyl betaine, oleyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like; amidobetaines and amidosulfobetaines, wherein the $\text{RCONH}(\text{CH}_2)_2$ radical is attached to the nitrogen atom of the betaine are also useful in this invention. Most preferred for use herein is cocoamidopropyl betaine.

The shampoo compositions of the present invention may further comprise additional deterative surfactants for use in combination with the anionic deterative surfactant component described hereinbefore. Suitable optional surfactants include nonionic surfactants, cationic surfactants, and combinations thereof. Any such surfactant known in the art for use in hair or personal care products may be used, provided that the optional additional surfactant is also chemically and physically compatible with the essential components of the shampoo composition, or does not otherwise unduly impair product performance, aesthetics or stability. Concentration of the optional additional surfactants in the shampoo composition

may vary with the cleaning or lather performance desired, the optional surfactant selected, the desired product concentration, the presence of other components in the composition, and other factors well known in the art.

Preferred for use are optional anionic deterative surfactants which can be used in addition to the alkyl ether sulfates are the water-soluble salts of organic, sulfuric acid reaction products of the general formula $[R_1-SO_3-M]$ where R_1 is selected from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 10 to about 18, carbon atoms; and M is a cation, as previously described, subject to the same limitations regarding polyvalent metal cations as previously discussed. Examples of such deterative surfactants are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g., SO_3 , H_2SO_4 , obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C_{10-18} n-paraffins.

Still other suitable anionic deterative surfactants are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil or palm kernel oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil or palm kernel oil. Other similar anionic surfactants are described in U.S. Patent 2,486,921; U.S. Patent 2,486,922; and U.S. Patent 2,396,278, which descriptions are incorporated herein by reference.

Other anionic deterative surfactants suitable for use in the shampoo compositions are the succinates, examples of which include disodium N-octadecylsulfosuccinate; disodium lauryl sulfosuccinate; diammonium lauryl sulfosuccinate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

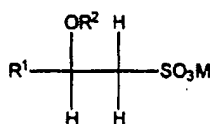
Other suitable anionic deterative surfactants include olefin sulfonates having about 10 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of alpha-olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO_2 , chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO_2 , etc., when used in the gaseous form.

The alpha-olefins from which the olefin sulfonates are derived are mono-olefins having about 10 to about 24 carbon atoms, preferably about 12 to about 16 carbon atoms. Preferably, they are straight chain olefins.

In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

5 A specific alpha-olefin sulfonate mixture of the above type is described more fully in the U.S. Patent 3,332,880, which description is incorporated herein by reference.

Another class of anionic deterative surfactants suitable for use in the shampoo compositions are the beta-alkyloxy alkane sulfonates. These compounds have the following formula:

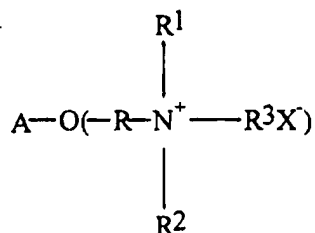


10 where R¹ is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R² is a lower alkyl group having from about 1 (preferred) to about 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

Preferred additional anionic deterative surfactants for use in the shampoo compositions include ammonium lauryl sulfate, ammonium laureth sulfate, triethylamine lauryl sulfate, triethylamine laureth sulfate, triethanolamine lauryl sulfate, triethanolamine laureth sulfate, monoethanolamine lauryl sulfate, monoethanolamine laureth sulfate, diethanolamine lauryl sulfate, diethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium lauryl sulfate, sodium laureth sulfate, potassium lauryl sulfate, potassium laureth sulfate, sodium lauryl sarcosinate, sodium lauroyl sarcosinate, lauryl sarcosine, cocoyl sarcosine, ammonium cocoyl sulfate, ammonium lauroyl sulfate, sodium cocoyl sulfate, sodium lauroyl sulfate, potassium cocoyl sulfate, potassium lauryl sulfate, triethanolamine lauryl sulfate, triethanolamine lauryl sulfate, monoethanolamine cocoyl sulfate, monoethanolamine lauryl sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, and combinations thereof.

Cationic Hair Conditioning Polymer

Cationic cellulosic derivative polymer materials suitable for use herein include those of the formula:



25

wherein: A is a cellulose anhydroglucose residual,

R is an alkylene, oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof,

R^1 , R^2 , and R^3 independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R^1 , R^2 and R^3) preferably being about 20 or less, and

5 X is an anionic counterion, as previously described.

The cationic cellulosic polymer has a molecular weight ranging from about 400,000 to about 1,500,000, preferably from about 500,000 to about 1,500,000 and most preferably from about 800,000 to about 1,200,000 and a charge density of from about 0.6 to about 3 meq/gr, preferably from about 0.7 to about 2.0 meq/gr. and most preferably from about 0.9 to about 1.5 meq/gr. Cationic cellulose is available
10 from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR and LR series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10.

The water soluble cationic described herein are either soluble in the shampoo composition, or preferably are soluble in a complex coacervate phase in the shampoo composition formed by the cationic
15 polymer and the anionic surfactant described hereinbefore. Complex coacervates of the cationic polymer can also be formed with other optional anionic components of the shampoo composition.

Coacervate formation is dependent upon a variety of criteria such as molecular weight, component concentration, and ratio of interacting ionic components, ionic strength (including modification of ionic strength, for example, by addition of salts), charge density of the cationic and anionic components, pH, and
20 temperature. Coacervate systems and the effect of these parameters have been described, for example, by J. Caelles, et al., "Anionic and Cationic Compounds in Mixed Systems", *Cosmetics & Toiletries*, Vol. 106, April 1991, pp 49-54, C. J. van Oss, "Coacervation, Complex-Coacervation and Flocculation", *J. Dispersion Science and Technology*, Vol. 9 (5,6), 1988-89, pp 561-573, and D. J. Burgess, "Practical Analysis of Complex Coacervate Systems", *J. of Colloid and Interface Science*, Vol. 140, No. 1, November
25 1990, pp 227-238, which descriptions are incorporated herein by reference.

It is believed to be particularly advantageous for the cationic polymer to be present in the shampoo composition in a coacervate phase, or to form a coacervate phase upon application or rinsing of the shampoo to or from the hair. Complex coacervates are believed to more readily deposit on the hair. Thus, in general, it is preferred that the cationic polymer exist in the shampoo composition as a coacervate phase
30 or form a coacervate phase upon dilution. If not already a coacervate in the shampoo composition, the cationic polymer will preferably exist in a complex coacervate form in the shampoo upon dilution with water.

Techniques for analysis of formation of complex coacervates are known in the art. For example, microscopic analyses of the shampoo compositions, at any chosen stage of dilution, can be utilized to
35 identify whether a coacervate phase has formed. Such coacervate phase will be identifiable as an

additional emulsified phase in the composition. The use of dyes can aid in distinguishing the coacervate phase from other insoluble phases dispersed in the shampoo composition.

Insoluble Hair Conditioning Agent

5 The shampoo compositions of the present invention further comprises an insoluble hair conditioning agent at concentrations effective to provide hair conditioning benefits. Such concentrations generally range from about 0.005% to about 5%, preferably from about 0.05% to about 4%, more preferably from about 0.1% to about 3.5%, most preferably from about 0.2% to about 3%, by weight of the shampoo compositions. The insoluble hair conditioning particles useful in the present invention have a particle size range below about 4 microns, preferably below about 1 micron, most preferably below about 10 0.5 microns. Useful conditioning agents include silicone and petrolatum.

Silicone Hair Conditioning Agent

Most preferred for use herein are non-volatile silicone conditioning agents. Typically it will be intermixed in the shampoo composition so as to be in the form of a separate, discontinuous phase of dispersed, insoluble particles, also referred to as droplets. These droplets may be suspended with a suspending agent described hereinafter. The silicone hair conditioning agent phase will comprise a silicone 15 fluid hair conditioning agent such as a silicone fluid and can also comprise other ingredients, such as a silicone resin to enhance silicone fluid deposition efficiency or enhance glossiness of the hair (especially when high refractive index (e.g. above about 1.46) silicone conditioning agents are used (e.g. highly phenylated silicones).

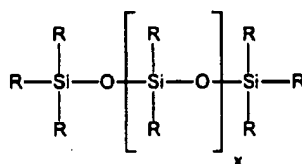
20 As used herein, "nonvolatile" refers to silicone material with little or no significant vapor pressure under ambient conditions, as is understood by those in the art. Boiling point under one atmosphere (atm) will preferably be at least about 250°C, more preferably at least about 275°C, most preferably at least about 300°C. Vapor pressure is preferably about 0.2mm HG at 25°C or less, preferably about 0.1mm HG at 25°C or less.

25 The silicone hair conditioning agent phase may comprise volatile silicone, nonvolatile silicone, or mixtures thereof. Typically, if volatile silicones are present, it will be incidental to their use as a solvent or carrier for commercially available forms of nonvolatile silicone materials ingredients, such as silicone gums and resins.

30 The silicone hair conditioning agents for use in the shampoo compositions preferably have a viscosity of from about 20 to about 2,000,000 centistokes, more preferably from about 1,000 to about 1,800,000 centistokes, even more preferably from about 10,000 to about 1,500,000 centistokes, most preferably from about 30,000 to about 1,000,000 centistokes, at 25°C. The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970.

Optional silicone fluid for use in the shampoo compositions includes silicone oil which are flowable silicone materials with a viscosity of less than 1,000,000 centistokes, preferably between about 5 and 1,000,000 centistokes, more preferably between about 10 and about 600,000 centistokes, more preferably between about 10 and about 500,000 centistokes, most preferably between 10 and 300,000 centistokes at 25°C. Suitable silicone oils include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other insoluble, nonvolatile silicone fluids having hair conditioning properties can also be used.

Optional Silicone oils for use in the composition include polyalkyl or polyaryl siloxanes which conform to following formula:



10

where R is aliphatic, preferably alkyl or alkenyl, or aryl, R can be substituted or unsubstituted, and x is an integer from 1 to about 8,000. Suitable unsubstituted R groups include alkoxy, aryloxy, alkaryl, arylalkyl, arylalkenyl, alkamino, and ether-substituted, hydroxyl-substituted, and halogen-substituted aliphatic and aryl groups. Suitable R groups also include cationic amines and quaternary ammonium groups.

15

The aliphatic or aryl groups substituted on the siloxane chain may have any structure as long as the resulting silicones remain fluid at room temperature, are hydrophobic, are neither irritating, toxic nor otherwise harmful when applied to the hair, are compatible with the other components of the shampoo compositions, are chemically stable under normal use and storage conditions, are insoluble in the shampoo compositions, and are capable of being deposited on and, of conditioning, the hair.

20

The two R groups on the silicon atom of each monomeric silicone unit may represent the same group or different groups. Preferably, the two R groups represent the same group.

Preferred alkyl and alkenyl substituents are C₁-C₅ alkyls and alkenyls, more preferably from C₁-C₄, most preferably from C₁-C₂. The aliphatic portions of other alkyl-, alkenyl-, or alkynyl-containing groups (such as alkoxy, alkaryl, and alkamino) can be straight or branched chains and preferably have from one to five carbon atoms, more preferably from one to four carbon atoms, even more preferably from one to three carbon atoms, most preferably from one to two carbon atoms. As discussed above, the R substituents hereof can also contain amino functionalities, e.g. alkamino groups, which can be primary, secondary or tertiary amines or quaternary ammonium. These include mono-, di- and tri- alkylamino and alkoxyamino groups wherein the aliphatic portion chain length is preferably as described above. The R substituents can also be substituted with other groups, such as halogens (e.g. chloride, fluoride, and bromide), halogenated aliphatic or aryl groups, and hydroxy (e.g. hydroxy substituted aliphatic groups). Suitable halogenated R groups could include, for example, tri-halogenated (preferably fluoro) alkyl groups

30

such as $-R^1-C(F)_3$, wherein R^1 is C_1-C_3 alkyl. Examples of such polysiloxanes include polymethyl -3,3,3-trifluoropropylsiloxane.

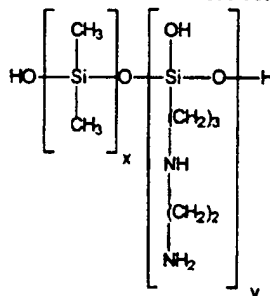
Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicones are polydimethyl siloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane is especially preferred. Other suitable R groups include methyl, methoxy, ethoxy, propoxy, and aryloxy. The three R groups on the end caps of the silicone may also represent the same or different groups.

The nonvolatile polyalkylsiloxane fluids that may be used include, for example, polydimethylsiloxanes. These siloxanes are available, for example, from the General Electric Company in their Viscasil R and SF 96 series, and from Dow Corning in their Dow Corning 200 series.

The polyalkylaryl siloxane fluids that may be used, also include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

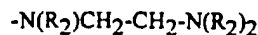
The polyether siloxane copolymers that may be used include, for example, a polypropylene oxide modified polydimethylsiloxane (e.g., Dow Corning DC-1248) although ethylene oxide or mixtures of ethylene oxide and propylene oxide may also be used. The ethylene oxide and polypropylene oxide level must be sufficiently low to prevent solubility in water and the composition hereof.

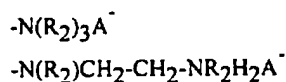
Suitable alkylamino substituted silicones include those conforming to the following formula:



wherein x and y are integers. This polymer is also known as "amodimethicone".

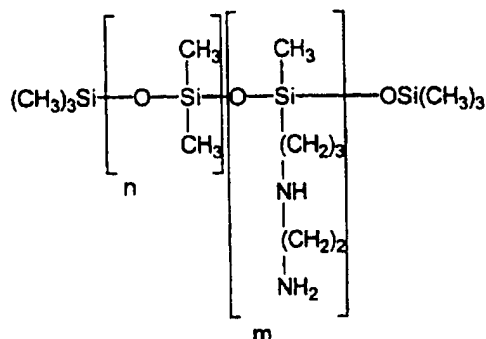
Suitable cationic silicone fluids include those conforming to the formula described hereinabove, wherein $(R_1)_a G_{3-a} \text{---Si---} (-\text{OSiG}_2)_n \text{---} (-\text{OSiG}_b (R_1)_2)_m \text{---O---SiG}_{3-a} (R_1)_a$ in which G is chosen from the group consisting of hydrogen, phenyl, OH, C_1-C_8 alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum $n+m$ is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R_1 is a monovalent radical of formula $C_q H_{2q} L$ in which q is an integer from 2 to 8 and L is chosen from the groups



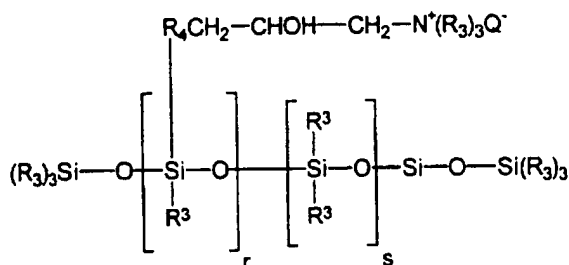


in which R_2 is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and A^- denotes a halide ion.

5 An especially preferred cationic silicone corresponding to the previous formula is the polymer known as "trimethylsilylamodimethicone", which conforms to the following formula:



Other silicone cationic polymers which can be used in the shampoo compositions are those which
10 conform to the following formula:



where R³ denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl; R₄ denotes a hydrocarbon radical, preferably a C₁-C₁₈ alkylene radical or a C₁-C₁₈, and more preferably C₁-C₈, alkyleneoxy radical; Q⁻ is a halide ion, preferably chloride; r denotes an average statistical value from 2 to 20, preferably from 2 to 8; s denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56."

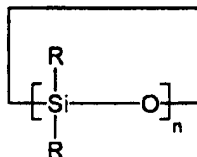
Other suitable silicone fluids for use in the silicone conditioning agents are insoluble silicone gums. These gums are polyorganosiloxane materials having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. Silicone gums are described in U.S. Patent 4,152,416; Noll and Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968; and in General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76, all of which are incorporated herein by reference. The silicone gums will typically have a mass molecular weight in excess of about 200,000, generally

between about 200,000 and about 1,000,000, specific examples of which include polydimethylsiloxane, (polydimethylsiloxane) (methylvinylsiloxane) copolymer, poly(dimethylsiloxane) (diphenyl siloxane)(methylvinylsiloxane) copolymer and mixtures thereof.

5 The silicone hair conditioning agent can also comprise a mixture of polydimethylsiloxane gum (viscosity greater than about 1,000,000 centistokes) and polydimethylsiloxane oil (viscosity from about 10 to about 100,000 centistokes), wherein the ratio of gum to fluid is from about 30:70 to about 70:30, preferably from about 40:60 to about 60:40.

Another category of nonvolatile, insoluble silicone fluid conditioning agents are high refractive index silicones, having a refractive index of at least about 1.46, preferably at least about 1.48, more preferably at least about 1.52, most preferably at least about 1.55. Although not intended to necessarily be limiting, the refractive index of the polysiloxane fluid will generally be less than about 1.70, typically less than about 1.60. Polysiloxane "fluid" includes oils as well as gums.

15 The high refractive index polysiloxane fluid suitable for purposes hereof includes those conforming to the formula described hereinabove, as well as cyclic polysiloxanes such as those conforming to the following formula:



wherein R is as defined above, n is from about 3 to about 7, preferably from 3 to 5.

20 The high refractive index polysiloxane fluids contain a sufficient amount of aryl-containing R substituents to increase the refractive index to the desired level, which is described above. In addition, R and n must be selected so that the material is nonvolatile, as defined above.

Aryl-containing substituents contain alicyclic and heterocyclic five and six membered aryl rings, and substituents containing fused five or six membered rings. The aryl rings themselves can be substituted or unsubstituted. Substituents include aliphatic substituents, and can also include alkoxy substituents, acyl substituents, ketones, halogens (e.g., Cl and Br), amines, etc. Exemplary aryl-containing groups include substituted and unsubstituted arenes, such as phenyl, and phenyl derivatives such as phenyls with C₁-C₅ alkyl or alkenyl substituents, e.g., allylphenyl, methyl phenyl and ethyl phenyl, vinyl phenyls such as styrenyl, and phenyl alkynes (e.g. phenyl C₂-C₄ alkynes). Heterocyclic aryl groups include substituents derived from furan, imidazole, pyrrole, pyridine, etc. Fused aryl ring substituents include, for example, naphthalene, coumarin, and purine.

30 In general, the high refractive index polysiloxane fluids will have a degree of aryl-containing substituents of at least about 15%, preferably at least about 20%, more preferably at least about 25%, even

more preferably at least about 35%, most preferably at least about 50%. Typically, although it is not intended to necessarily limit the invention, the degree of aryl substitution will be less than about 90%, more generally less than about 85%, preferably from about 55% to about 80%.

5 The polysiloxane fluids are also characterized by relatively high surface tensions as a result of their aryl substitution. In general, the polysiloxane fluids hereof will have a surface tension of at least about 24 dynes/cm², typically at least about 27 dynes/cm². Surface tension, for purposes hereof, is measured by a de Nouy ring tensiometer according to Dow Corning Corporate Test Method CTM 0461, November 23, 1971. Changes in surface tension can be measured according to the above test method or according to ASTM Method D 1331.

10 Preferred high refractive index polysiloxane fluids have a combination of phenyl or phenyl derivative substituents (preferably phenyl), with alkyl substituents, preferably C₁-C₄ alkyl (most preferably methyl), hydroxy, C₁-C₄ alkylamino (especially -R¹NHR²NH₂ where each R¹ and R² independently is a C₁-C₃ alkyl, alkenyl, and/or alkoxy. High refractive index polysiloxanes are available from Dow Corning Corporation (Midland, Michigan, U.S.A.) Huls America (Piscataway, New Jersey, U.S.A.), and General Electric Silicones (Waterford, New York, U.S.A.).

15 It is preferred to utilize high refractive index silicones in solution with a spreading agent, such as a silicone resin or a surfactant, to reduce the surface tension by a sufficient amount to enhance spreading and thereby enhance glossiness (subsequent to drying) of hair treated with the composition. In general, a sufficient amount of the spreading agent to reduce the surface tension of the high refractive index polysiloxane fluid by at least about 5%, preferably at least about 10%, more preferably at least about 15%,
20 even more preferably at least about 20%, most preferably at least about 25%. Reductions in surface tension of the polysiloxane fluid/spreading agent mixture can provide improved shine enhancement of the hair.

Also, the spreading agent will preferably reduce the surface tension by at least about 2 dynes/cm²,
25 preferably at least about 3 dynes/cm², even more preferably at least about 4 dynes/cm², most preferably at least about 5 dynes/cm².

The surface tension of the mixture of the polysiloxane fluid and the spreading agent, at the proportions present in the final product, is preferably 30 dynes/cm² or less, more preferably about 28 dynes/cm² or less most preferably about 25 dynes/cm² or less. Typically the surface tension will be in the
30 range of from about 15 to about 30, more typically from about 18 to about 28, and most generally from about 20 to about 25 dynes/cm².

The weight ratio of the highly arylated polysiloxane fluid to the spreading agent will, in general, be between about 1000:1 and about 1:1, preferably between about 100:1 and about 2:1, more preferably between about 50:1 and about 2:1, most preferably from about 25:1 to about 2:1. When fluorinated surfactants are used, particularly high polysiloxane: spreading agent ratios may be effective due to the efficiency of these surfactants. Thus it is contemplated that ratios significantly above 1000:1 may be used.

References disclosing examples of some suitable silicone fluids for use in the shampoo compositions include U.S. Patent 2,826,551, U.S. Patent 3,964,500, U.S. Patent 4,364,837, British Patent 849,433, and Silicon Compounds, Petrarch Systems, Inc. (1984), all of which are incorporated herein by reference.

Silicone resins can be included in the silicone conditioning agent. These resins are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of trifunctional and tetrafunctional silanes with monofunctional or difunctional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units (and hence, a sufficient level of crosslinking) such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinyl-chlorosilanes, and tetrachlorosilane, with the methyl-substituted silanes being most commonly utilized. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art.

Background material on silicones including sections discussing silicone fluids, gums, and resins, as well as manufacture of silicones, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons, Inc., 1989, incorporated herein by reference.

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as "MDTQ" nomenclature. Under this system, the silicone is described according to presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the monofunctional unit $(\text{CH}_3)_3\text{SiO}_{.5}$; D denotes the difunctional unit $(\text{CH}_3)_2\text{SiO}$; T denotes the trifunctional unit $(\text{CH}_3)\text{SiO}_{1.5}$; and Q denotes the quadri- or tetra-functional unit SiO_2 . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other

than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyls, amines, hydroxyls, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone (or an average thereof) or as specifically indicated ratios in combination with molecular weight complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MDT and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

The weight ratio of the nonvolatile silicone fluid, having refractive index below 1.46, to the silicone resin component, when used, is preferably from about 4:1 to about 400:1, preferably this ratio is from about 9:1 to about 200:1, more preferably from about 19:1 to about 100:1, particularly when the silicone fluid component is a polydimethylsiloxane fluid or a mixture of polydimethylsiloxane fluid and polydimethylsiloxane gum as described above. Insofar as the silicone resin forms a part of the same phase in the compositions hereof as the silicone fluid, i.e. the conditioning active, the sum of the fluid and resin should be included in determining the level of silicone conditioning agent in the composition.

The shampoo composition of the present invention may further comprise a suspending agent for the insoluble conditioning agent. Such suspending agents are well known in the shampoo and conditioning art. Examples of some suitable suspending agents are described in U.S. Patent 4,741,855, U.S. Patent 4,788,006, U.S. Patent 4,704,272, U.S. Patent 2,798,053, which descriptions are incorporated herein by reference. Suitable suspending agents for use in combination with the insoluble conditioning agent include acyl derivatives, long chain amine oxides, xanthan gum, and carboxyvinyl polymers. Other suitable suspending agents include primary amines having a fatty alkyl moiety having at least about 16 carbon atoms, secondary amines having two fatty alkyl moieties each having at least about 12 carbon atoms, di(hydrogenated tallow)phthalic acid amide, and crosslinked maleic anhydride-methyl vinyl ether copolymer.

Other suitable suspending agents for use in combination with the insoluble conditioning agent include those that can impart a gel-like viscosity to the composition, such as water soluble or colloiddally water soluble polymers like cellulose ethers (e.g., methylcellulose, hydroxybutyl methylcellulose, hydroxypropylcellulose, hydroxypropyl methylcellulose, hydroxyethyl ethylcellulose and hydroxyethylcellulose), guar gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives, and other thickeners, viscosity modifiers, gelling agents, and so forth.

The shampoo compositions of the present invention comprise a low viscosity, organic conditioning oil which is solubilized in the surfactant component as an additional hair conditioning agent for use in combination with the cationic hair conditioning polymer described hereinbefore. The concentration of the low viscosity, organic oil ranges from about 0.05% to about 3%, preferably from about 0.08% to about 1.5%, more preferably from about 0.1% to about 1%, by weight of the shampoo composition.

The low viscosity, organic, conditioning oils are water insoluble, water dispersible, liquids selected from the group consisting of hydrocarbon oils and fatty esters, or combinations thereof, wherein the organic conditioning oil has a viscosity of from about 1 to about 300 centipoise, preferably from about 1 to about 150 centipoise, more preferably from about 2 to about 50 centipoise, as measured at 40°C according to ASTM D-445.

It has been found that these low viscosity organic conditioning oils provide the shampoo composition with improved conditioning performance when used in combination with the essential components of the composition. These organic conditioning oils are believed to be solubilized in the surfactant micelles of the shampoo composition. It is also believed that this solubilization into the surfactant micelles contributes to the improved hair conditioning performance of the shampoo compositions herein.

Suitable organic conditioning oils for use in the shampoo composition include hydrocarbon oils having at least about 10 carbon atoms, such as cyclic hydrocarbons, straight chain aliphatic hydrocarbons (saturated or unsaturated), and branched chain aliphatic hydrocarbons (saturated or unsaturated), including polymers thereof. Straight chain hydrocarbon oils preferably contain from about 12 to about 19 carbon atoms. Branched chain hydrocarbon oils, including hydrocarbon polymers, can and typically will contain more than 19 carbon atoms. Specific non limiting examples of these hydrocarbon oils include paraffin oil, mineral oil, saturated and unsaturated dodecane, saturated and unsaturated tridecane, saturated and unsaturated tetradecane, saturated and unsaturated pentadecane, saturated and unsaturated hexadecane, polybutene, polydecene, and combinations thereof. Branched-chain isomers of these compounds, as well as of higher chain length hydrocarbons, can also be used, examples of which include highly branched, saturated or unsaturated, alkanes such as the permethyl-substituted isomers, e.g., the permethyl-substituted isomers of hexadecane and eicosane, such as 2, 2, 4, 4, 6, 6, 8, 8-dimethyl-10-methylundecane and 2, 2, 4, 4, 6, 6-dimethyl-8-methylnonane, sold by Permethyl Corporation. Hydrocarbon polymers such as polybutene and polydecene, especially polybutene, can also be used.

Other organic conditioning oils for use in the shampoo composition include a liquid polyolefin such as a liquid polyalphaolefin or a hydrogenated liquid polyalphaolefin. Polyolefins for use in the shampoo composition herein are prepared by polymerization of olefinic monomers containing from about 4 to about 14 carbon atoms, preferably from about 6 to about 12 carbon atoms. Polyalphaolefins are preferred, and

are prepared by polymerization of 1-alkene monomers having from about 4 to about 14 carbon atoms, preferably from about 6 to about 12 carbon atoms.

Non limiting examples of olefinic monomers for use in preparing the polyolefin liquids herein include ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, branched chain isomers such as 4-methyl-1-pentene, and combinations thereof. Also suitable for preparing the polyolefin liquids are olefin-containing refinery feedstocks or effluents. Preferred, however, are the hydrogenated alpha-olefin monomers having from about 4 to about 14 carbon atoms, or combinations thereof, examples of which include 1-hexene to 1-hexadecenes and combinations thereof, and preferably are 1-octene to 1-tetradecene or combinations thereof.

10

Water

The shampoo compositions of the present invention comprise from about 20% to about 94%, preferably from about 50% to about 94%, more preferably from about 60% to about 85%, by weight of water.

Other Optional Components

15

The shampoo compositions of the present invention may further comprise one or more optional components known for use in shampoo or conditioning compositions, provided that the optional components are physically and chemically compatible with the essential component described herein, or do not otherwise unduly impair product stability, aesthetics or performance. Concentrations of such optional components typically range from about 0.001% to about 10% by weight of the shampoo compositions.

20

Optional components include anti static agents, dyes, organic solvents or diluents, pearlescent aids, foam boosters, additional surfactants or cosurfactants (nonionic, cationic, zwitterionic), pediculocides, pH adjusting agents, perfumes, preservatives, proteins, skin active agents, suspending agents, styling polymers, sunscreens, thickeners, vitamins, and viscosity adjusting agents. This list of optional components is not meant to be exclusive, and other optional components can be used.

25

Method of Manufacture

The shampoo compositions of the present invention can be prepared by using various formulation and mixing techniques or methods known in the art for preparing surfactant or conditioning compositions, or other similar compositions.

Method of Use

30

The shampoo compositions of the present invention are used in a conventional manner for cleansing and conditioning hair or skin. An effective amount of the composition for cleansing and conditioning the hair or skin is applied to the hair or skin, that has preferably been wetted with water, and then rinsed off. Such effective amounts generally range from about 1g to about 50g, preferably from about 1g to about 20g. Application to the hair typically includes working the composition through the hair such that most or all of the hair is contacted with the composition.

35

This method for cleansing and conditioning the hair comprises the steps of:

- a) wetting the hair with water, b) applying an effective amount of the shampoo composition to the hair, and c) rinsing the shampoo composition from the hair using water. These steps can be repeated as many times as desired to achieve the desired cleansing and conditioning benefit.

5

Examples

The shampoo compositions illustrated in Examples I-XV illustrate specific embodiments of the shampoo compositions of the present invention, but are not intended to be limiting thereof. Other modifications can be undertaken by the skilled artisan without departing from the spirit and scope of this invention. These exemplified embodiments of the shampoo compositions of the present invention provide
10 cleansing of hair and improved hair conditioning performance.

All exemplified compositions can be prepared by conventional formulation and mixing techniques. Component amounts are listed as weight percents and exclude minor materials such as diluents, filler, and so forth. The listed formulations, therefore, comprise the listed components and any minor materials associated with such components.

<u>Component</u>	<u>Example Number</u>				
	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>
Ammonium Laureth-3 Sulfate	14.00	14.00	14.00	14.00	14.00
Cocamidopropylbetaine	2.70	2.70	2.70	2.70	2.70
Polyquaternium-10 (3)	0.15	0.15	0.15	0.30	0.30
Light Mineral Oil	0.30	0.15	0.05	0.30	0.15
Cocamide MEA	0.80	0.80	0.80	0.80	0.80
Cetyl Alcohol	0.42	0.42	0.42	0.42	0.42
Stearyl Alcohol	0.18	0.18	0.18	0.18	0.18
Ethylene Glycol Distearate	1.50	1.50	1.50	1.50	1.50
Dimethicone (1)	1.00	1.00	1.00	3.00	1.00
Perfume Solution	0.70	0.70	0.70	0.70	0.70
DMDM Hydantoin	0.37	0.37	0.37	0.37	0.37
Color Solution (ppm)	64	64	64	64	64
Water and Minors					
	----- q.s. to 100% -----				

<u>Component</u>	<u>Example Number</u>				
	<u>VI</u>	<u>VII</u>	<u>VIII</u>	<u>IX</u>	<u>X</u>
Ammonium Laureth-3 Sulfate	14.00	11.75	12.50	14.85	12.50
Cocamidopropylbetaine	2.70	2.25	4.20	1.85	4.20
Polyquaternium-10 (3)	0.30	0.15	0.15	0.15	0.30
Light Mineral Oil	0.60	0.30	0.15	0.60	0.30
Cocamide MEA	0.80	0.80	0.80	0.80	0
Cetyl Alcohol	0	0.42	0.42	0.42	0.42
Stearyl Alcohol	0	0.18	0.18	0.18	0.18
Ethylene Glycol Distearate	1.50	1.50	1.50	1.50	1.50
Dimethicone (1)	1.00	3.00	1.00	1.00	1.00
Perfume Solution	0.70	0.70	0.70	0.70	0.70
DMDM Hydantoin	0.37	0.37	0.37	0.37	0.37
Color Solution (ppm)	64	64	64	64	64

Water and Minors

----- q.s. to 100% -----

ComponentExample Number

	<u>XI</u>	<u>XII</u>	<u>XIII</u>	<u>XIV</u>	<u>XV</u>
Ammonium Laureth-3 Sulfate	14.00	14.00	14.00	10.00	10.00
Cocamidopropylbetaine	2.70	2.70	2.70	2.00	2.00
Polyquaternium-10 (3)	0.15	0.15	0.30	0.10	0.10
Polybutene (4)	0.15	0.30	0.30	0.10	0.20
Cocamide MEA	0.80	0.80	0	0.80	0.60
Cetyl Alcohol	0	0.42	0	0.42	0
Stearyl Alcohol	0	0.18	0	0.18	0
Ethylene Glycol Distearate	0	0	0	1.50	1.50
Carbopol 981 (2)	0.50	0.50	0.50	0	0
Dimethicone (1)	1.00	1.00	1.00	1.00	0.50
Perfume Solution	0.70	0.70	0.70	0.70	0.70
DMDM Hydantoin	0.37	0.37	0.37	0.37	0.37
Color Solution (ppm)	64	64	64	64	64
Water and Minors					

----- q.s. to 100% -----

(1) Dimethicone is an emulsion of 60,000 csk polydimethyl siloxane with particle size of approximately 300 nm available from Dow Corning (DC 1664).

(2) Carbopol 981 is a crosslinked polyacrylate available from B.F. Goodrich.

(3) Polyquaternium-10 is UCare Polymer JR30M from Amerchol.

(4) Polybutene is Indopol L-14 from Amoco.

What is claimed is:

1. An aqueous shampoo composition comprising:

- 5 a) from 5.0% to 50% of a surfactant component comprising:
- i) an ethoxylated alkyl sulfate surfactant having from 1 to 8 moles of ethoxylation; and
- ii) an amphoteric surfactant;
- b) from 0.01% to 3.0% of a cationic cellulosic polymer having a molecular weight of from 400,000
- 10 to 1,500,000 and charge density of from 0.6meq/gram to 3meq/gram, preferably 0.7meq/gram to
- 2meq/gram, more preferably 0.9meq/gram to 1.5meq/gram;
- c) from 0.005% to 5%, preferably 0.05% to 4%, more preferably 0.2% to 3%, of a water insoluble
- non-volatile silicone conditioning agent having an average particle size below 4 microns;
- d) from 0.05% to 5%, by weight, of an organic, nonvolatile, water insoluble liquid which is
- 15 solubilized in the surfactant component and having a viscosity of from 1 to 300 centipoise selected
- from the group consisting of hydrocarbon oils and fatty esters having a boiling point at ambient
- pressure of 250°C or higher, and mixtures thereof; and
- e) an aqueous carrier

wherein said composition comprises less than 5% of ethoxylated alkyl sulfate surfactant having less than 1 mole of ethoxylation.

20

2. An aqueous shampoo composition according to Claim 1 which comprises from 8% to 30% of said surfactant component and wherein said composition comprises less than 3% of ethoxylated surfactant having less than 1 mole of ethoxylation and wherein said amphoteric surfactant is cocoamidopropyl betaine and wherein said non-volatile conditioning agent is a silicone.

5

3. A aqueous shampoo composition according to any one of the preceding Claims, wherein said component (d) is selected from the group consisting of straight and branched chain hydrocarbon oils and fatty esters having at least 20 carbon atoms, and mixtures thereof.
4. A aqueous shampoo composition according to any one of the preceding Claims, wherein said component (d) has a viscosity of 150 cS or less at 40°C.
5. A aqueous shampoo composition according to any one of the preceding Claims, wherein said fatty esters are selected from the group consisting of alkyl and alkenyl esters of fatty acids, alkyl and alkenyl esters of fatty alcohols, polyhydric alcohol esters, dicarboxylic acid esters, tricarboxylic acid esters, and mono-, di-, and tri-glycerides, and mixtures thereof.
6. An aqueous shampoo composition according to any one of the preceding Claims, wherein said nonvolatile silicone conditioning agent is selected from the group consisting of polyarylsiloxanes, polyalkyl siloxanes, polyalkylarylsiloxanes, derivatives thereof, and mixtures thereof, preferably polydimethylsiloxane.
7. An aqueous shampoo composition according to any one of the preceding Claims, wherein nonvolatile silicone conditioning agent has an average particle size of less than 1 micron, preferably less than 0.5 microns.
8. An aqueous shampoo composition according to any one of the preceding Claims, wherein said cationic cellulosic polymer hair conditioning agent is Polyquaternium-10.
9. An aqueous shampoo composition according to any one of the preceding Claims, wherein said amphoteric surfactant is cocoamidopropyl betaine and comprises from 1% to 10%, preferably 2% to about 5% of the composition.
10. An aqueous shampoo composition according to any one of the preceding Claims, wherein said cationic polymer hair conditioning agent has a molecular weight of from 800,000 to 1,200,000.

INTERNATIONAL SEARCH REPORT

Inter. Application No
PCT/US 97/03698

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/075

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93 08787 A (PROCTER & GAMBLE) 13 May 1993 see page 8, line 5 - page 33, line 25; claims 1-9; examples IV,V -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

7 August 1997

Date of mailing of the international search report

14.08.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Willekens, G

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 97/03698

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9308787 A	13-05-93	AT 141784 T	15-09-96
		AU 674834 B	16-01-97
		AU 2927292 A	07-06-93
		BR 9206689 A	02-05-95
		CA 2120492 A	13-05-93
		CN 1072589 A	02-06-93
		CZ 9401025 A	19-10-94
		DE 69213247 D	02-10-96
		DE 69213247 T	27-03-97
		EP 0610407 A	17-08-94
		ES 2090702 T	16-10-96
		FI 941969 A	28-04-94
		HU 67994 A	14-03-95
		JP 7500609 T	19-01-95
		NO 941535 A	28-06-94
		NZ 244925 A	21-12-95
		PT 101011 A	28-02-94
		SK 46094 A	08-03-95